PATENT SPECIFICATION

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NO DRAWINGS.

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COMPLETE SPECIFICATION.

Process for the Preparation of Hydrocarbon Oils, Entirely or Substantially Entirely Freed from Mercaptans.

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ, N.V., a Company organised under the Laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of hydrocarbon oils entirely or substantially entirely freed from mercaptans, by treating a hydrocarbon oil containing mercaptans with one or more copper compounds, preferably in the presence of oxygen. The fundamental reactions taking place in the course of this type of sweetening process are the same in principle for various copper compounds. In the case of cupric chloride the course of these reactions may be represented as follows:—

$$4\ RSH + 4\ CuCl_2 \longrightarrow 2\ RSSR + 4\ CuCl + 4\ HCl$$

$$4\ CuCl + 4\ HCl + O_2 \longrightarrow 4\ CuCl_2 + 2\ H_2O$$

Thus the overall reaction amounts to:—

$$4\ RSH + O_2 \longrightarrow 2\ RSSR + 2\ H_2O$$

In the above equations R refers to a hydrocarbon group.

In principle this sweetening process is very attractive since, owing to their cupric-cuprous form, the copper compounds serve solely as an oxidation medium. It follows from the above reactions that theoretically there is no consumption of chemicals other than oxygen.

However, when the process is carried out in practice, small quantities of copper compounds are taken up in the hydrocarbon oil treated, which is a serious draw-back as even traces of copper compounds have a very unfavourable effect on the stability of the hydrocarbon oil. In order to eliminate these small quantities of copper compounds it has been proposed to subject the sweetened hydrocarbon oil to an after-treatment with, for example, a solution of sodium sulphide. It has been found, however, that the after-treatments hitherto proposed are not sufficiently effective or, as in the case of the use of sodium sulphide, lead to problems of entrainment of sodium compounds.

According to the present invention a process for the preparation of a hydrocarbon oil entirely or substantially entirely freed from mercaptans comprises treating a mercaptan-containing hydrocarbon oil with one or more copper compounds, preferably in the presence of oxygen, to free it entirely or substantially entirely from mercaptans and then subjecting it to an after-treatment with an adsorbent impregnated with hydrochloric acid to eliminate traces of copper compounds wholly or substantially.

The elimination of mercaptans by means of a treatment with copper compounds may be effected in various ways. For example, the hydrocarbon oil to be sweetened may be contacted with an aqueous solution of a copper compound, such as cupric chloride. In this case, the reduced copper solution is usually regenerated by means of oxygen after the separation of the sweetened hydrocarbon oil.

It is preferred, however, to perform the treatment with a solid support material on which are supported one or more copper compounds. The quantities of copper compound taken up by the sweetened hydro-

carbon oil are then usually smaller than in the case of a treatment with a solution of copper compounds. The use of a solid support material containing copper permits the sweetening and the regeneration of the cuprous compound into a cupric compound in a simple manner by means of a single treatment. To this end, the hydrocarbon oil is contacted with the support material in the presence of oxygen. The support material is used either in the form of a fixed bed or a slurry in the hydrocarbon oil. When it is used as a slurry the hydrocarbon oil is intimately contacted for some time with the support material. The support material is then separated from the sweetened hydrocarbon oil in a separator, after which it may again be contacted with fresh quantities of hydrocarbon oil. Should the hydrocarbon oil to be sweetened contain hydrogen sulphide and/or other acid components, such as phenols and thiophenols, it is advisable to eliminate them entirely or in part by a preliminary treatment, for example by means of a caustic wash.

Examples of suitable hydrocarbons are the fractions obtained by straight-run distillation of crude oil, and the hydrocarbon oils obtained by the thermal or catalytic cracking or by reforming. The sweetening treatment is particularly suitable for light hydrocarbon oils, such as gasoline and kerosene, and to fractions containing normally gaseous components, e.g. fractions containing propane/propene and butane/butene. The process is also suitable for use in the treatment of gas oils.

Oxygen, or a gas containing oxygen, such as air, may be used for the regeneration of the reduced copper compound, although use may also be made of such peroxides as ozone, which form oxygen under the reaction conditions. The oxygen is preferably introduced before the sweetening treatment, for instance by injection of pressurized air into the hydrocarbon oil.

Preferred copper compounds are cupric chloride and/or mixtures of cupric sulphate and sodium or ammonium chloride.

Suitable support materials are such adsorbents as activated carbon, fuller's earth and pumice, on which relatively large quanitites of copper compound may be supported, e.g. by impregnating them with an aqueous solution of copper salt, such that preferably the copper content of fresh absorbent is 1—10% weight.

It should be noted that the activity of the support material charged with copper is determined, inter alia, by a specific water content (4—20%) of the support material charged with the copper compound, but the activity may substantially decline when the support material adsorbs much larger quantities of water. For this reason it is important that the starting hydrocarbon oil should contain little free water, e.g. about 100 p.p.m. of water. The use of a hydrocarbon oil not saturated with water ensures a prolonged activity of the support material containing copper, since the reaction water formed by the oxidation of the mercaptans into disulphides will be absorbed by the hydrocarbon oil to be treated, which is not saturated with water.

All or substantially all traces of copper compound taken up in the hydrocarbon oil as a result of the sweetening treatment, can be eliminated in a simple and effective manner by means of the after-treatment of the sweetened hydrocarbon oil with an adsorbent impregnated with hydrochloric acid.

This after-treatment, which may be batchwise or continuous, is carried out, for example, by slurrying in the hydrocarbon oil the adsorbent impregnated with preferably 1—10% hydrochloric acid by weight. In a continuous process the hydrocarbon oil may, for example, be introduced into the bottom of a column countercurrently to the adsorbent introduced at the top of the column, but the after-treatment is preferably effected by passing the hydrocarbon oil over a fixed bed of an adsorbent impregnated with hydrochloric acid.

Suitable adsorbents include activated carbon, silica gel and fuller's earth. Activated carbon gives particularly good results.

An advantage of the after-treatment is that it eliminates not only the traces of copper compounds but also any oxidation products formed, as well as all the nitrogen bases.

The temperatures at which the sweetening treatment and the after-treatment for the elimination of traces of copper compounds are carried out, are usually in the range of from 10° to 80° C., although temperatures between 20° and 65° C. are preferred. At slightly higher temperatures it is possible to use higher space velocities and obtain the same results.

During the sweetening treatment the liquid hourly space velocities usually vary from 10 to 25 l./l/h, as is also the case during the after-treatment for eliminating the copper compounds.

In practicing the process use will generally be made of two columns when fixed beds are employed. The first column is packed with a support material charged with one or more copper-compounds, and the second with an adsorbent impregnated with hydrochloric acid. The support material and the adsorbent may be the same product, e.g. activated carbon.

A particularly attractive embodiment is that in which one column only is used, its upper part being filled with activated carbon on which one or more copper compounds,

for example cupric chloride, is supported, and the lower part being filled with activated carbon impregnated with hydrochloric acid. When the hydrocarbon oil to be sweetened, together with oxygen or an oxygen-containing gas, is introduced into the top of the column, the mercaptans are converted into disulphides in the upper part; in the lower part will be adsorbed the traces of copper compounds taken up by the hydrocarbon oil when the latter is passed through the upper part.

After a prolonged use of this column, the dissolution of small quantities of the copper compounds solution in the hydrocarbon oil will cause a decline in activity of the activated carbon on which the cupric chloride is supported. As soon as the activity has so declined that traces of copper compounds leave the bottom of the column, the direction of the flow of the hydrocarbon oil may be reversed, i.e. the hydrocarbon oil to be sweetened is now introduced into the bottom of the column, so that traces of copper compounds dissolved are returned to the upper part of the column where the cupric chloride was leached out by prolonged use.

It should be noted that during the process hydrochloric acid may be added to the column if necessary.

In certain cases it may be advantageous to subject the hydrocarbon oil before the sweetening treatment to a light treatment with an acid, such as hydrochloric acid. This can be done very suitably by passing the hydrocarbon oil to be sweetened over activated carbon impregnated with hydrochloric acid. This preliminary treatment eliminates traces of metallic compounds, such as iron and zinc compounds, as well as certain basic reaction compounds. The elimination of these compounds prolongs the activity of the adsorbent impregnated with a copper compound of which use is made for sweetening.

Example.

The starting material is a straight-run kerosene having the characteristics mentioned in column A of the Table. This kerosene is successively led through two columns. The first column, having a diameter of 7.5 cm., was filled to a height of 65 cm. with an activated carbon on which cupric chloride was supported. The second column had a diameter of 7.5 cm. and was filled to a height of 65 cm. with an activated carbon impregnated with hydrochloric acid. The carbon-containing copper had been prepared by washing with water activated carbon of which the granules had an average diameter of 0.7 mm.; this carbon was subsequently impregnated with an aqueous solution of 6% cupric chloride and then dried. The copper content was 3% by weight. The carbon impregnated with hydrochloric acid was prepared by washing with cold water activated carbon of which the granules had an average diameter of 0.7 mm., until it was neutral. After being immersed in an aqueous solution of 1 N hydrochloric acid the carbon-containing hydrochloric acid was dried for 24 hours at approximately 105° C.

The kerosene previously saturated at the ambient temperature by injection of air was slightly heated and introduced at 35° C. into the top of the first column. The liquid hourly space velocity was 20 l./l./h. The kerosene leaving this column was almost free from mercaptans (mercaptan sulphur content <3 p.p.m.) and contained 2 p.p.m. of copper. This kerosene was then led into the top of the second column at a liquid hourly space velocity of 20 l./l./h. The kerosene leaving the column had a copper content of less than 0.01 p.p.m. The characteristics of the kerosene are specified in column B of the Table.

Kerosine	A not treated	B after column II
Boiling range (A.S.T.M., °C.)	173—222	173—222
Density at 15° C.	0.789	0.789
Total sulphur, %	0.184	0.183
RSH sulphur, %	0.017	<0.0005
Alkyl phenols, mg./l	144	110
Char value		12.7
Copper (p.p.m.)	0.05	0.01
Potential gum		0.6
Nitrogen base	2.6	1.2
Thermal Stability Test (Thermal Stability of Aviation Turbine Fuels; ASTM—CFR Fuel Coker Test D 1660—59T) ...		
Δ P (Pressure drop across the filter) ...		
Preheater tube deposit rating		0.5
Corrosion (ASTM—D130)		1.A
Acid number (ASTM D974—58T) ...		0.0035

The invention also embraces hydrocarbon oils entirely or substantially entirely freed from mercaptans by the process of the invention.

WHAT WE CLAIM IS:—

1. A process for the preparation of a hydrocarbon oil entirely or substantially entirely freed from mercaptans, by treating a mercaptan-containing hydrocarbon oil with one or more copper compounds characterized in that the hydrocarbon oil which is entirely or substantially entirely freed from mercaptans is subjected to an after treatment with an absorbent impregnated with hydrochloric acid to eliminate traces of copper compounds wholly or substantially.

2. A process as claimed in Claim 1 in which the treatment with the copper compound or compounds is performed in the presence of oxygen.

3. A process as claimed in Claim 1 or Claim 2 in which the absorbent impregnated with hydrochloric acid is in the form of a contact bed.

4. A process as claimed in Claim 1 or Claim 2 or Claim 3 in which the absorbent is activated carbon or silica gel or fuller's earth.

5. A process as claimed in any of the preceding claims in which the treating temperatures employed are in the range of from 20° to 65° C.

6. A process as claimed in any of the preceding claims in which the hydrocarbon oil containing mercaptans is passed with oxygen from the top to the bottom of a single column of which the upper part is filled with activated carbon containing one or more copper compounds and the lower part is filled with activated carbon impregnated with hydrochloric acid.

7. A process as claimed in Claim 6 which includes adding hydrochloric acid to the column.

8. A process as claimed in any of the preceding claims which includes subjecting the hydrocarbon oil containing mercaptans to a preliminary treatment with a caustic alkali solution to eliminate hydrogen sulphide and/or other acid compounds.

9. A process as claimed in any of the preceding claims which includes subjecting the hydrocarbon oil containing mercaptans to a preliminary treatment with an absorbent impregnated with hydrochloric acid to eliminate traces of metal compounds.

10. A process as claimed in any of the preceding claims in which the hydrocarbon oil containing mercaptans is not saturated with water.

11. A process for the production of hydrocarbon oil entirely or substantially entirely freed from mercaptans substantially as described in the foregoing example.

12. A hydrocarbon oil entirely or substantially entirely freed from mercaptans by a process as claimed in any of the preceding claims.

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Chartered Patent Agents,
Agents for the Applicants.

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